

## PHOSPHITE ESTER ADDITIVE COMPOSITIONS

This application claims priority from United States provisional patent application serial number 60/273,303 filed March 2, 2001, United States provisional patent application serial number 60/314,181 filed August 16, 2001, and United States provisional patent application serial number 60/315,746 filed August 29, 2001.

### **Technical Field**

The invention relates generally to improving the performance and reducing the heavy metal content of PVC compounds by the partial or total substitution of conventional mixed metal stabilizers with phosphite esters, or blends thereof, with an effective amount of added zinc.

## ***Background of the Invention***

The PVC industry began with the invention of plasticized polyvinyl chloride ("PVC") by Waldo Semon of the B. F. Goodrich Company in 1933 as an alternative to natural rubber where its non-flammability made it ideal for wire insulation, particularly on naval ships. However, unlike rubber, PVC has a tendency to discolor and is not easy to process well. Stabilization is required to perform two basic functions: (1) prevent discoloration; and (2) absorb hydrogen chloride (HCl) which evolves during process. It is believed that billions of pounds of flexible PVC are employed throughout the world in a wide variety of commercial applications. These include vinyl flooring, wall covering, roofing, pond and pool liners, film, upholstery, apparel, hose, tubing and wire insulation.

In order to successfully process vinyl compounds into finished vinyl articles by extrusion, calendering or molding, it is necessary to incorporate between one and five percent of a heat stabilizer to prevent dehydrohalogenation and discoloration of the polymer during thermal processing. The preferred vinyl heat stabilizers for most flexible PVC applications in the United States are referred to as "Mixed Metal" heat stabilizers. They are complex multi-component chemical admixtures based upon combinations of alkaline earth and heavy metal salts with a variety of antioxidants, HCl absorbers and chelating agents. The most widely used mixed metals are based upon and referred to as Barium-Cadmium, Barium-Cadmium-Zinc, Barium-Zinc and Calcium-Zinc stabilizers. However, mixed metal heat stabilizers suffer from several drawbacks. If the level of zinc is too high, the polymer will char very rapidly. Additionally, barium and cadmium are toxic heavy metals which while they do provide heat stability, their presence adversely affects

1 clarity, plate out and stain. In order to counteract these negative effects, further additional  
2 components were blended into the formulations, making PVC additive formulation and  
3 processing a highly unique and specialized art. Clearly, what was needed was an  
4 approach which used higher performance phosphites and added back only what was  
5 needed.

1        These and other objects of the present invention will become more readily apparent  
2    from a reading of the following detailed description taken in conjunction with the  
3    accompanying drawings wherein like reference numerals indicate the parts and appended  
4    claims.

5        ***Brief Description of the Drawings***

6        The invention may take physical form in certain parts and arrangements of parts, a  
7    preferred embodiment of which will be described in detail in the specification and illustrated  
8    in the accompanying drawings which form a part hereof, and wherein:

9        FIG. 1 is a graph over time of the impact on oven aging by varying the class of  
10   phosphite stabilizer used to stabilize PVC (as measured by Yellowness Index) using 100  
11   parts PVC resin, 45 parts dioctyl phthalate, 20 parts  $\text{CaCO}_3$ , 5 parts epoxidized soybean  
12   oil, 0.25 parts stearic acid, 0.2 parts zinc stearate, and 2 parts of various classes of  
13   phosphites;

14       FIG. 2 is a graph over time of the impact of oven aging by varying the amount of  
15   added zinc used with diphenyl ethylhexyl phosphite (as measured by Yellowness Index)  
16   using 100 parts PVC resin, 45 parts dioctyl phthalate, 20 parts  $\text{CaCO}_3$ , 5 parts epoxidized  
17   soybean oil, 0.25 parts stearic acid, 2 parts diphenyl ethylhexyl phosphite, and various  
18   amounts of zinc stearate;

19       FIG. 3 is a graph over time of the impact on oven aging by varying the amount of  
20   tetraisodecyl bisphenol A diphosphite used to stabilize PVC (as measured by Yellowness  
21   Index) using 100 parts PVC resin, 45 parts dioctyl phthalate, 20 parts  $\text{CaCO}_3$ , 5 parts  
22   epoxidized soybean oil, and 0.2 parts zinc stearic acid and various amounts of bisphenol A-  
23   based phosphite;

24       FIG. 4 is a graph over time of the impact on oven aging by varying the phosphite or  
25   phosphite blend used to stabilize PVC (as measured by Yellowness Index) using 100 parts  
26   PVC resin, 45 parts dioctyl phthalate, 20 parts  $\text{CaCO}_3$ , 5 parts epoxidized soybean oil, and  
27   0.25 parts stearic acid, 0.25 parts zinc stearate and 2.0 parts phosphite or phosphite blend;

28       FIG. 5 is a graph over time of the impact on oven aging by comparing a phosphite of  
29   the instant invention (i.e., tetraisodecyl bisphenol-A diphosphite / poly DPG phenyl  
30   phosphite blend with 2.5% zinc octanoate) to Prior Art PVC stabilizers (as measured by  
31   Yellowness Index) using 100 parts PVC resin, 25 parts dioctyl phthalate, 25 parts  $\text{CaCO}_3$ ,  
32   3 parts epoxidized soybean oil, 7.0 parts  $\text{TiO}_2$ , and 0.5 parts stearic acid and 4 parts of  
33   stabilizer;

1 FIG. 6 is a graph over time of the impact on the QUV weathering test by comparing  
2 a phosphite of the instant invention (i.e., tetraisodecyl bisphenol-A diphosphite / poly DPG  
3 phenyl phosphite blend containing 2.5% zinc octanoate) to Prior Art PVC stabilizers (as  
4 measured by Yellowness Index) using 100 parts PVC resin, 55 parts 7-11, 3 parts  
5 epoxidized soybean oil, 7.0 parts TiO<sub>2</sub>, and 0.3 parts stearic acid and 3.5 parts of stabilizer;  
6 and

7 FIG. 7 is a bar chart of percentage weight loss of various stabilizers and a phosphite  
8 ester blend of the present invention after 2 hours at 110°C illustrated in Table VI.

9 ***Detailed Description of the Invention***

10 Referring now to the drawings wherein the showings are for purposes of illustrating  
11 the preferred embodiment of the invention only and not for purposes of limiting the same,  
12 the Figures show various comparisons of phosphite ester / Zn additive compositions with  
13 that of various Prior Art additives. As illustrated in FIG. 1, the efficacy of all classes of  
14 phosphites is not equivalent. The hydrogen phosphites are the least effective class of  
15 phosphite esters, whereas the bisphenol-A phosphites as well as the dipropylene glycol  
16 phosphites showed extended resistance to yellowing over time. Within each class of  
17 phosphite, the performance for particular phosphites was very similar.

18 The level of zinc present in the stabilizer affects the performance of the additive. As  
19 noted in the Prior Art, early color is improved with added zinc. However, as shown in FIG.  
20 2, a window of optimum zinc level exists, the specific range of the window being somewhat  
21 unique for each phosphite class. If the zinc concentration is too low, the early color will not  
22 be acceptable. If the zinc concentration is too high, the PVC will char at earlier exposure  
23 times. This effect is displayed for an alkyl-aryl phosphite (i.e., diphenyl ethylhexyl  
24 phosphite) in FIG. 2, although the relationship is demonstrated for all classes of phosphite  
25 esters.

26 Although the zinc level has an optimum value for effectiveness, the level of  
27 phosphite does not appear to be as sensitive. In general, the long-term color improved with  
28 an increase in the level of phosphite as shown in FIG. 3. The increase in phosphite level  
29 (i.e., Doverphos® 675, a C<sub>10</sub> bisphenol A phosphite) had little effect on the color of the PVC  
30 strip before 50 minutes, but extended the final char time to greater than 120 minutes.  
31 Again, this trend was observed for most classes of phosphites. Thus phosphites can  
32 replace other heavy metal stabilizers by complexing acidic Zn, in addition to reacting with  
33 labile chlorides and HCl.

1       Synergistic effects were observed using combinations of phosphite classes. FIG. 4  
2    displays blends of alkyl-aryl, DPG and BPA based phosphites. The total concentration of  
3    phosphite remained constant at 2.0 parts. It is obvious that the addition of a higher